GEOPHYSICAL RESEARCH LETTERS, VOL. 23, NO. 17, PAGES 2373-2376, AUGUST 15, 1996

Stratospheric NO and NO_2 abundances from ATMOS solar-occultation measurements

M. J. Newchurch[1], M. Allen[2], M. R. Gunson[2], R. J. Salawitch[2], G. B. Collins[1], K. H. Huston[1], M. M. Abbas[3] M. C. Abrams[5] A. Y. Chang[2], D. W. Fahey[6], R. S. Gao[6], F. W. Irion[4], M. Loewenstein[7], G. L. Manney[2], H. A. Michelsen[8], J. R. Podolske[7], C. P. Rinsland[9], R. Zander[10]

Abstract. Using results from a time-dependent photochemical model to calculate the diurnal variation of NO and NO_2, we have corrected Atmospheric Trace MOlecule Spectroscopy (ATMOS) solar-occultation retrievals of the NO and NO_2 abundances at 90° solar zenith angle. Neglecting to adjust for the rapid variation of these gases across the terminator results in potential errors in retrieved profiles of ~20% for NO_2 and greater than 100% for NO at altitudes below 25 km. Sensitivity analysis indicates that knowledge of the local O_3 and temperature profiles, rather than zonal mean or climatological conditions of these quantities, is required to obtain reliable retrievals of NO and NO_2 in the lower stratosphere. Extremely inaccurate O_3 or temperature values at 20 km can result in 50% errors in retrieved NO or NO_2. Mixing ratios of NO in the mid-latitude, lower stratosphere measured by ATMOS during the November 1994 ATLAS-3 mission compare favorably with in situ ER-2 observations, providing strong corroboration of the reliability of the adjusted space-borne measurements.

Introduction

The rapid temporal variation in the concentrations of NO and NO_2 at sunrise and sunset, if not properly accounted for, will produce errors in the retrieval of these gases from solar-occultation measurements [Kerr et al., 1977; Boughner et al., 1980; Roscoe and Pyle, 1987; Russell et al., 1988]. We demonstrate that the correction for temporal variation is sufficiently sensitive to profiles of temperature and O_3 that local values of these quantities, rather than zonal or climatological means, are necessary to return accurate profiles of NO and NO_2. A coincidence between ATMOS and the NOAA NO-NO_y sensor on the ER-2 during November 1994 reveals good agreement between corrected NO profiles measured by ATMOS and in situ measurements in the lower stratosphere.

[1] University of Alabama in Huntsville, Huntsville, AL
[2] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA
[3] Marshall Space Flight Center, Huntsville, AL
[4] California Institute of Technology, Pasadena, CA
[5] SAIC - NASA Langley Research Center, Hampton, VA
[6] NOAA Aeronomy Laboratory, Boulder, CO
[7] NASA Ames Research Center, Moffett Field, CA
[8] Harvard University, Cambridge, MA
[9] NASA Langley Research Center, Hampton, VA
[10] University of Liège, Liège, Belgium

Paper number 96GL01196
0094-8534/96/96GL-01196$05.00

Sensitivity of correction factors to adopted parameters

The variation of NO and NO_2 near the terminator is governed primarily by the reaction of NO with O_3 and by the photolysis of NO_2. Hence, accurate knowledge of the local values of O_3, temperature (due to the temperature dependence of NO + O_3), and the radiation field is required to calculate the variation of NO and NO_2 across the terminator. We used the Caltech/JPL one-dimensional, time-dependent photochemical model [Allen and Delitsky, 1990, 1991] to calculate the diurnal variation of NO and NO_2. As a validation of our model calculations, we compared the computed variation of NO and NO_2 with observed diurnal variation at several altitudes and geophysical conditions [Kondo et al., 1989, 1990; Kawa et al., 1990; Webster et al., 1990]. In all cases, the agreement was very good. For example, Figure 1 shows a comparison of NO measurements at 20 km [Kawa et al., 1990] with the results of the model constrained by the measurements of O_3 and temperature simultaneous with NO. With both model results and measurements normalized by the volume mixing ratio (VMR) at solar zenith angle (SZA) of 90°, the agreement is excellent. The accuracy with which the model calculates the relative variation of NO and NO_2 is the critical element for correcting solar-occultation retrievals. We calculated factors describing the diurnal variation of NO and NO_2 relative to the values at SZA=90° (either sunrise or sunset) at 0.01° increments and subsequently smoothed to 0.1° increments for use in the ATMOS onion-peeling reduction algorithm [Norton and Rinsland, 1991] following the methodology of Murcray et al. [1978] and Rinsland et al. [1984]. This methodology applies the calculated factors to the measured slant columns during the onion-peeling retrieval process.

Sample model calculations show that the variation of NO and NO_2 at the terminator is not sensitive to assumptions concerning the local values of NO_y, H_2O, CH_4, the rates of heterogeneous reactions, or albedo variation. The sensitivities to prescribed O_3 and temperature, however, are large enough to require using O_3 and temperature measurements obtained simultaneously with the NO_x (=NO+NO_2) measurements to yield accurate, retrieved profiles. For example, an error of +/-50% in model O_3 at all altitudes results in an error in retrieved NO at SZA=90° of -10/-55% [NO] and +12/-55% [NO_2] at 20 km. Model errors of +/-25% in temperature result in somewhat smaller retrieval errors. These perturbations encompass potentially real deviations from climatological or zonal mean conditions; however, in the winter vortex, larger excursions may occur. The sensitivity to uncertainty in the adopted values for model calculations of both O_3 and temperature increases with decreasing altitude below 30 km. Because of the convolved effects of kinetics, photolysis, and slant-column geometry, however, the sensitivity is not always monotonic in

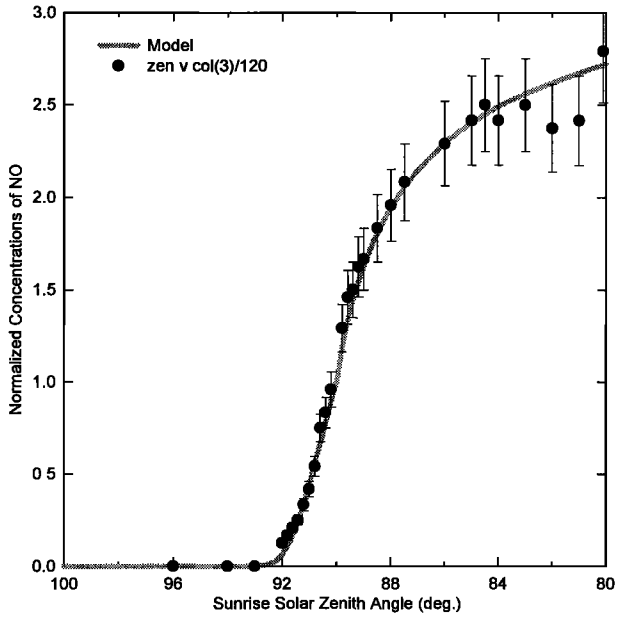

Figure 1. Kawa et al., [1990] ER-2 measurements (circles with 1σ error bars) of NO VMR normalized to the 90° solar zenith angle compared with results of a model simulation (grey line). The measurements occurred at 20 km and 39° N.

altitude. Simultaneous departures in both O_3 and temperature generally compound the resulting error in the gas profile, but not necessarily in a simple fashion. We note that some solar occultation experiments either ignore the effects of diurnal variation (e.g., SAGE NO_2 [Chu and McCormick, 1986 and Kerr et al., 1977]) or use a monthly, zonal-mean atmosphere for the correction computation (e.g., HALOE NO and NO_2 [J. M. Russell III, personal communication]).

Implications for ATMOS retrievals

NO profiles

Figure 2a displays the profiles of NO using three different treatments of the diurnal correction. ATLAS-3/SS01 (first sunset occultation) obtained at 49° N is a typical mid-latitude sunset occultation with an O_3 profile significantly different from the zonal-mean O_3, but with temperatures similar to the zonal mean. The retrieval that ignores the effects of diurnal variation (denoted NC) is the lowest of the three in the 10 to 30-km region. The retrieval that uses correction factors from a model employing simultaneously acquired ATMOS O_3 and temperature profiles (denoted PC) produces the highest values of NO. A retrieval using model results based on zonal-mean profiles of O_3 and temperature (denoted ZC) is intermediate to the other NO profiles. The PC retrieval abundances exceed 1σ NC measurement uncertainties between 16 and 18 km and also between 24 and 30 km. Figure 2b shows retrieved profiles of NO for sunrise occultation ATLAS-3/SR09 (sunrise number 9) in the southern hemisphere vortex. The NC retrieval yields roughly 50% of the amount of NO at 20 km compared to the PC retrieval. The ZC retrieval profile is quite similar to, and equally inaccurate as, the NC profile. The failure of the ZC retrieval is due to the extreme zonal variation of O_3 and temperature at these latitudes, which encompass the polar vortex [Manney et al., this issue]. As shown in the fractional difference between PC and NC, the correction exceeds the 1-sigma measurement uncertainty (dotted line) between 16 and 28 km. We also used the photochemical reconstruction model of Salawitch et al. [1994] to compute correction factors and obtained retrieved profiles of NO and NO_2 that differ from the PC values shown in Figures 2 and 3 by no more than 20%, significantly less than the uncertainty of the ATMOS measurement.

Similar analysis of other sunrise and sunset occultations reveals that the difference between PC and NC retrievals vary widely among the occultations, but that significant corrections do not occur above 30 km. Below 25 km, the true NO values may be as much as a factor of 5 larger than uncorrected values. Under some circumstances (e.g., at high latitudes, 72.3° S, in SR68 where the maximum SZA is only 91.7°) the PC profile values are actually less than the uncorrected profile values. No clear differences between sunrise and sunset corrections emerge.

NO_2 profiles

The effect of ignoring the diurnal variation of NO_2 in the retrieval process is in the opposite sense and of smaller magnitude

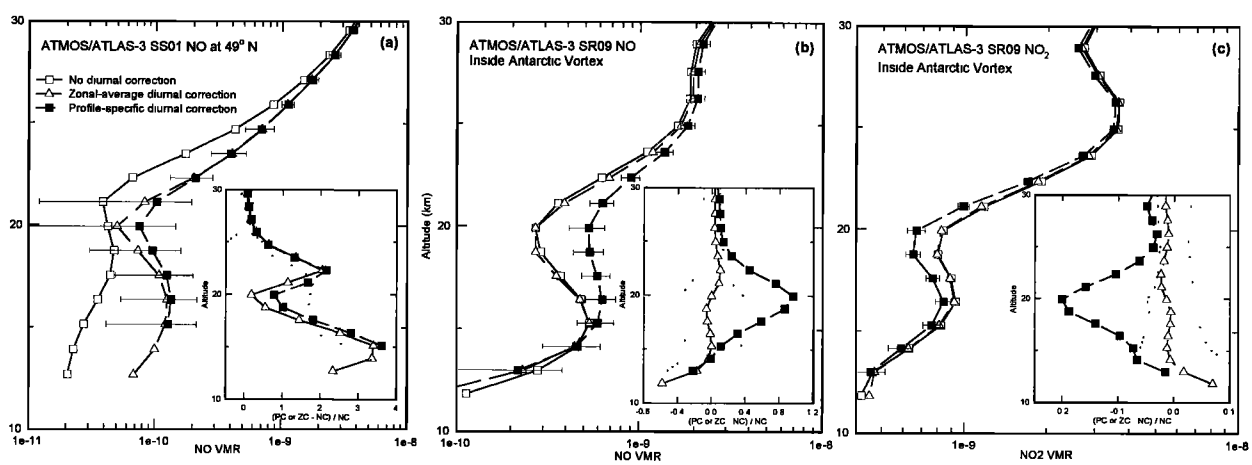

Figure 2. Retrieved profiles for NO and NO_2 without correction (NC denoted with open squares), with corrections computed from zonal-mean conditions (ZC denoted with open triangles), and with corrections computed from simultaneously measured conditions (PC denoted with solid squares) ±1σ precision. The insets show ZC and PC values relative to the NC values with dotted lines representing 1σ NC measurement uncertainties. Panel 2(a) shows the sunrise 09 profile inside the SH polar vortex. Panel 2(b) shows the sunset 01 profile with significant corrections of 200% and 350% at 22 km and 15 km, respectively. Panel 2(c) shows PC, ZC, and NC profiles for NO_2 in occultation SR09. Note that these corrections are in the direction opposite to the NO corrections.

than for NO. For example, as illustrated in Figure 2c for ATMOS/ATLAS-3 SR09, the accurately corrected NO_2 abundances (PC) are typically 10-20% lower than uncorrected amounts (NC), well in excess of the measurement uncertainties. Also, the approximate correction, ZC, is nearly the same as the NC profile. In another case, ATMOS/ATLAS-3 SS01 (not shown), both PC and ZC profiles are ~20% lower than the NC profile near 20 km. These corrections are in the same sense, but of greater magnitude, than previous estimates of approximately 5-10% [Kerr et al., 1977; Russell et al., 1988], possibly because of differences in time (or SZA) resolution of the model calculations. While the ZC corrections are typically 0-50% of the PC adjustments, sometimes the ZC correction exceeds the PC adjustment. Above 40 km, we find that PC profiles for NO_2 are typically lower that NC profiles (as has been illustrated for the lower stratosphere), but the corrections (less than 10%) are smaller than in the lower stratosphere. In addition, the corrections in the upper stratosphere are typically smaller than the measurement uncertainties at those altitudes and smaller than one previous estimate [Russell et al., 1988].

NO_x profiles

The sum of diurnally corrected NO and NO_2 amounts does not necessarily equal the sum of uncorrected NO_x. This difference is due to uncertainties in the inversion process; it is not a property of the model chemistry, which does conserve NO_x to better than 3% at 20 km, for example. Typically, the difference between corrected and uncorrected NO_x profiles varies by ± 15%, roughly the measurement precision at 20 km. This difference diminishes with increasing altitude, approaching zero at 30 km (above which altitude both NO and NO_2 corrections become insignificant.) Below 20 km, where both NO and NO_2 corrections increase in magnitude, the difference between corrected and uncorrected NO_x can be as large as 40% in the few occultations we have examined. However, the absolute magnitude of the correction does not exceed 0.2 ppbv at any altitude, a small fraction of the NO_y (=NO + NO_2 + HNO_3 + $ClONO_2$ + HNO_4 + 2*N_2O_5) budget.

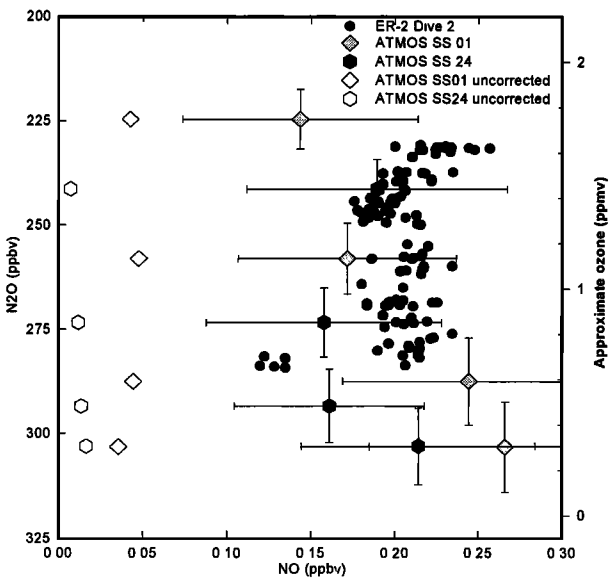

Figure 3. Comparison of ATMOS/ATLAS-3 NO measurements with results of the NO-NO_y NOAA instrument on board the ER-2 during ASHOE/MAESA (dive 2) on November 4, 1994. Both SS01 and SS24 have been diurnally corrected as described in the text and scaled to the ER-2 solar zenith angle of 72°. Error bars on ATMOS NO and N_2O reflect estimates of the 1-σ measurement precision

ER-2 comparisons

Some of the sunset occultation measurements obtained during the early days of the ATMOS ATLAS-3 mission occurred within 1 day and roughly coincident in space with in situ measurements of NO on 4 November 1994, during the ASHOE/MAESA ER-2 campaign. SS01 and SS24, while respectively 1 day before and 1 day after the ER-2 observations on 4 November, yielded correlations of O_3 and N_2O very similar to the in situ observations [Chang et al., this issue]. Chang et al. demonstrate good agreement between ATMOS and in-situ measurements of correlations between NO_y and N_2O. Figure 3 illustrates a comparison of the space-borne ATMOS and in situ measurements of NO [Fahey et al., 1989] as a function of the long-lived tracer N_2O [Lowenstein et al., 1989] to account for variations in the precursors (O_3 and NO_y) that regulate levels of NO_x in the sampled air masses. The NC ATMOS profile values (open symbols) are shown for reference. We used the photochemical model to adjust the PC profiles (not shown) for SS01 and SS24 to account for the change in NO from SZA=90° to the ER-2 solar conditions of mid-day at SZA=72°. The scaling from 90° to mid-day is approximately a factor of two at all altitudes reported in figure 3. The good agreement between calculated and observed variation in NO with changing solar illumination illustrated in Figure 1 provides confidence in the fidelity of the scaling used to estimate the mid-day values of NO from the ATMOS sunset measurements. The agreement between NO measured by ATMOS and the NOAA NO-NO_y instrument shown in Figure 3 is well within the ATMOS 1-σ precision error bars. The systematic error in these measurements is estimated to be 5% for NO. The accuracy of the ER-2 NO measurements is 15% with precision of 0.02 ppbv.

The ATMOS temperatures were approximately 5-10 K lower than the ER-2 temperatures at all altitudes. Adjustment for this temperature difference would lower the ATMOS NO values by approximately 10-30% due to the temperature dependence of the rate of NO + O_3, which increases with increasing temperature. This adjustment would degrade the agreement somewhat. At the lowest part of dive 2 (pressures greater than 100mb), the ER-2 encountered higher temperatures and lower values of NO. These lower NO values cluster around an average value of 0.1 ppbv at 280 ppbv N_2O. In situ measurements with temperatures greater than 223 K are unrepresentative of the comparable air mass and, therefore, are not shown in Figure 3. Five points of the low-NO cluster remain in Figure 3. 12-Day back trajectory calculations initialized at 420 and 465 K indicate that air at the locations of SS01 and SS24, and at a number of ER-2 measurement locations, has similar history, having been drawn into mid-latitudes from the subtropics. However, at 465 K, air from some of the ER-2 measurement locations compared here, appears to have come from mid-latitudes around the developing vortex. A more complete comparison of spaceborne and in situ measurements of NO requires accounting for the latitude and temperature histories of the air parcels, an analysis beyond the scope of this paper.

Conclusions

Adjustments to NO profiles retrieved from solar-occultation observations for the effects of rapid abundance variation near the terminator become significant below ~25-28 km, typically 100-200%, but sometimes as large as 500%. The adjustment to NO_2 solar-occultation profiles is smaller than for NO; the adjustment becomes significant below ~30 km and is ~20% at 20 km (well in excess of the 5-10% estimate currently accepted.) These results use model calculations adopting profiles for O_3 and temperature measured simultaneously with the NO and NO_2 observations. Because the adjustment for diurnal variation is a strong function of atmospheric ozone amount and temperature (and the resulting species concentrations as a function of solar zenith angle) for a wide range of NO_x levels, adjustments to the NO and NO_2 retrievals using model calculations initialized with zonal mean or climatological O_3 and temperature profiles may be quite different (and erroneous). NO_x profiles based on the sum of corrected retrieved NO and NO_2 are typically different from NO_x based on uncorrected retrievals, ~15% at 20 km, but sometimes as high as 40% at 16 km. When adjusted for differences in solar illumination at times of measurement, corrected ATMOS/ATLAS-3 values for NO between 17 and 20 km are in good agreement with in situ, ER-2 measurements. This agreement suggests that the remotely sensed measurement of NO is reliable within its stated error bars, even at a mixing-ratio level two orders of magnitude and 25 km below the peak in the stratospheric profile.

Acknowledgments. This work was supported in part by the NASA Atmospheric Chemistry Modeling and Analysis Program, NASA/MSFC Earth Sciences and Applications Division contract NAS8-38609, and JPL-959894. Work at the Jet Propulsion Laboratory, California Institute of Technology was done under contract with the National Aeronautics and Space Administration. Partial support was received from NASA grant NAGW-1538 to the California Institute of Technology.

References

Allen, M., and M. L. Delitsky, Stratospheric NO, NO_2, and N_2O_5: A comparison of model results with Spacelab 3 Atmospheric Trace Molecule Spectroscopy measurements, *J. Geophys. Res.*, 95, 14,077-14,082, 1990.

Allen, M., and M. L. Delitsky, A test of odd-oxygen photochemistry using Spacelab 3 Atmospheric Trace Molecule Spectroscopy observations, *J. Geophys. Res.*, 96, 12,883-12,891, 1991.

Boughner, R., J. C. Larsen, and M. Natarajan, The influence of NO and ClO variations at twilight on the interpretation of solar occultation measurements, *Geophys. Res. Lett.*, 7, 231-234, 1980.

Chang et al., A comparison of measurements from ATMOS and the ER-2: Tracers of atmospheric transport, *Geophys. Res. Lett.*, this issue.

Chu, W. P., and M. P. McCormick, SAGE observations of stratospheric nitrogen dioxide, *J. Geophys. Res.*, 91, 5465-5476, 1986.

Fahey, D. W. et al., In situ measurements of total reactive nitrogen, total water, and aerosol in a polar stratospheric cloud in the Antarctic, *J. Geophys. Res.*, 94,11,299-11,315, 1989.

Kawa, S. R. et al., Interpretation of aircraft measurements of NO, ClO, and O_3 in the lower stratosphere, *J. Geophys. Res.*, 95, 18,597-18,609, 1990.

Kerr, J. B., W. F. J. Evans, and J. C. McConnell, The effects of NO_2 changes at twilight on tangent ray NO_2 measurements, *Geophys. Res. Lett.*, 4, 577-579, 1977.

Kondo, Y., N. Toriyama, W. A. Matthews, and P. Aimedieu, Calibration of the balloon-borne NO instrument, *J. Geomag. Geoelectr.*, 41, 507-523, 1989.

Kondo, Y. et al., Diurnal variation of nitric oxide in the upper stratosphere, J. *Geophys. Res.*, 95, 22,513-22,522, 1990.

Loewenstein, M., J. R. Podolske, K. R. Chan, and S. E. Strahan, Nitrous oxide as a dynamical tracer in the 1987 Airborne Antarctic Ozone Experiment, *J. Geophys. Res.*, 94, 11,589-11,598, 1989.

Manney, G. L., R. Swinbank, and A. O'Neill, Stratospheric Meteorological conditions for the 3-12 Nov. 1994 ATMOS/ATLAS-3 measurements, *Geophys. Res. Lett.* ,this issue.

Michelangeli, D. V., M. Allen, and Y. L. Yung, El Chichon volcanic aerosols: Impact of radiative, thermal and chemical perturbations, *J. Geophys. Res.*, 94, 18,429-18,443, 1989.

Murcray, D. G., A. Goldman, G. R. Cook, D. K. Rolens, and L. R. Megill, On the interpretation of infrared solar spectra for altitude distribution of atmospheric trace constituents, *FAA-EE-78-30,* Department of Transportation Federal Aviation Administration Office of Environment and Energy, University of Denver, Denver, Colorado, 1978.

Norton, R. H. , and C. P. Rinsland, ATMOS data processing and science analysis methods, *Appl. Opt.*, 30, 389-400, 1991.

Rinsland, C. P., R. E. Boughner, J. C. Larsen, G. M. Stokes, and J. W. Brault, Diurnal variations of atmospheric nitric oxide: Ground-based infrared spectroscopic measurements and their interpretation with time-dependent photochemical model calculations, J. Geophys. Res., 89, 9613-9622, 1984.

Roscoe, H. K. and J. A. Pyle, Measurements of solar occultation: the error in a naive retrieval if the constituent's concentration changes, J. Atmos. Chem., 5 , 323-341, 1987.

Russell III, J. M. et al., Measurements of odd nitrogen compounds in the stratosphere by the ATMOS experiment on Spacelab 3, J. Geophys. Res., 93, 1718-1736, 1988.

Salawitch, R. J. et al., The diurnal variation of hydrogen, nitrogen, and chlorine radicals: Implications for the heterogeneous production of HNO_2, Geophys. Res. Lett., 21, 2551-2554, 1994.

Webster, C. R., R. D. May, R. Toumi, and J. A. Pyle, Active nitrogen partitioning and the nighttime formation of N_2O_5 in the stratosphere: Simultaneous in situ measurements of NO, NO_2, HNO_3, O_3, and N_2O using the BLISS diode laser spectrometer, J. Geophys. Res., 95, 13,851-13, 866, 1990.

M. J. Newchurch, Earth System Science Laboratory, U. Alabama in Huntsville, Huntsville, AL, 35899, USA.(mike@ozone.atmos.uah.edu)

(Received October, 17, 1995; revised March, 8, 1996; accepted March 22, 1996.)